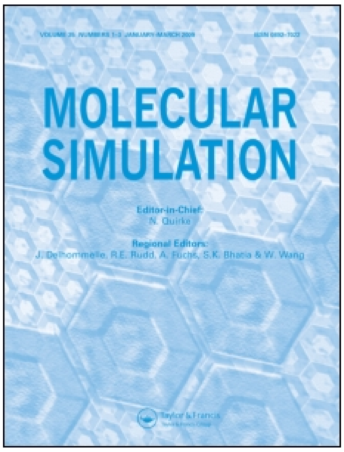

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H. Yan[a]; Y. C. Shi[b]; G. Liu[a]; S. L. Yuan[a]
[a] Key Laboratory of Colloid and Interface Chemistry, Shandong University, Jinan, P. R. China [b] School of Material Science and Engineering, Shandong University, Jinan, People's Republic of China

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Theoretical calculation on the reaction of alkene molecules on H-terminated Si(100)-3 × 1 surface

H. Yan[a], Y.C. Shi[b]*, G. Liu[a] and S.L. Yuan[a]*

[a]*Key Laboratory of Colloid and Interface Chemistry, Shandong University, Jinan, P. R. China;* [b]*School of Material Science and Engineering, Shandong University, Jinan, People's Republic of China*

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A study on mechanisms of radical initiated surface chain reaction of ethylene molecule on H-terminated Si(100)-3 × 1 has been carried out in a supercell approach by using density functional theory and *ab initio* molecular dynamic method. On the H-terminated Si(100)-3 × 1 surface, one of the crucial steps of the surface chain reaction, namely, the abstraction of a H atom from a nearby surface hydride unit, is found to have a somewhat smaller activation energy from the nearest silicon site than from the next-nearest silicon site. From the intermediate state to the final state, the transition state has bigger activation energy. *Ab initio* molecular dynamics (MD) shows that the H-abstraction on Si(100)-3 × 1 surface bound organic group with a carbon-centered radical is very easy to be obtained from the transition state, and it also shows that the C···H bond at methyl group is formed in a very short MD time, and the Si···C bond between the Si surface and the alkyl chain oscillates with time evolution on Si(100)-3 × 1 surface.

Keywords: silicon; density functional calculation; linear synchronous transit; *ab initio* molecular dynamics

1. Introduction

Organic modifications of silicon surfaces by attachments of various unsaturated molecules have been attracting much attention for further advancement in biosensor or semiconductor technology. From the beginning works of Chidsey et al. [1,2], several methods have been developed to obtain the close-packed monolayer on Si surface, involving both wet chemical and ultrahigh-vacuum approaches [3–12]. Among these, a promising way is the radical initiated reaction of unsaturated 1-alkene molecules with the hydrogen-terminated silicon surfaces [13–17]. It is widely accepted that the growth mechanism consists of two main steps [18]. First, the organic molecule reacts with a previously generated Si dangling bond and binds to the surface through a Si—C bond, giving rise to a metastable surface bound organic group with a carbon-centered radical (named as intermediate); then, this highly reactive carbon radical abstracts a hydrogen atom from a neighbouring Si—H group to produce a new silicon dangling bond, which can act as attachment site for another molecule, thus leading to a surface chain reaction. Such a procedure has been applied to grow the organic monolayer on the H-terminated Si(111), H-terminated Si(100) and the porous silicon [19–22].

Many experiments have proven the radical chain mechanism through the reactions of organic molecules including styrene, propylene, octane and others on H-Si(111) or H-Si(000) surface [23–26]. And density functional theory (DFT) calculations have been performed on reactions of 1-alkene molecules with Si(111) or Si(100) surface on the basis of cluster models and periodic slab models [27–29]. In addition, molecular mechanics and molecular dynamics (MD) of the alkyl monolayers on the surface have also been carried out, and much valuable information is provided for the experimentalists [30–35].

Different Si(100) crystals are found in nature, such as Si(100)-3 × 1 and −2 × 1. Since the Si(100) − 3 × 1 crystal has two Si—H bonds on one Si atom besides the dimers between other Si atoms on H-terminated surface (please see the structure in scheme 1, and the Si(100)-2 × 1 surface has only dimers), in this present work, we will focus on the effect of the two Si—H bonds to the H-abstractions on H-terminated Si(100) − 3 × 1 surface, and discuss the possible reaction pathways of ethylene molecule through the transition state using the DFT and *ab initio* MD methods. The radical chain reaction mechanism on Si(100) − 3 × 1 surface is shown in scheme 1. From the intermediate state to the product, the question is which hydrogen atom should be abstracted from the same dimer (I) or the near single Si atom (II)?

In our calculations, we always assume that on unsaturated Si dangling bond is initially present on the surface. Using the linear synchronous transit (LST) method [36] for finding chemical reaction pathways, the structures and energies of the intermediates and transition states of the addition reaction are discussed in detail,

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*Corresponding authors. Emails: yuanchangshi@sdu.edu.cn; shilingyuan@sdu.edu.cn

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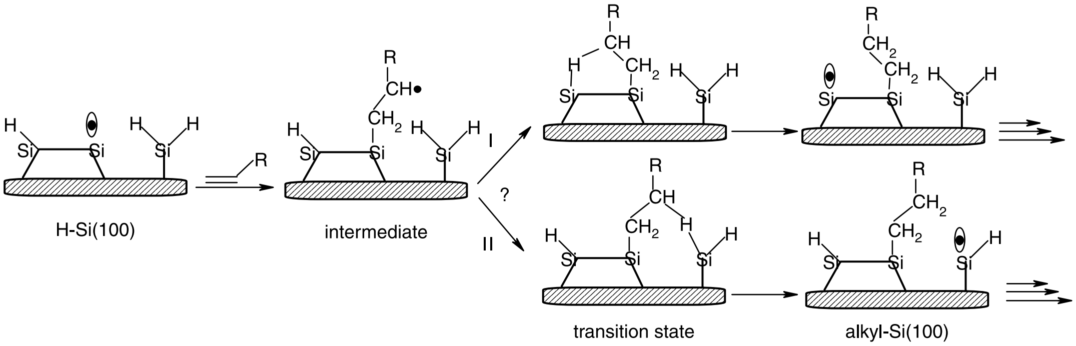

Scheme 1. Radical chain reaction including the pathways of H-abstraction on Si(100)-3 × 1 surface.

which are important aspects not easily accessed by experiments. And we investigate how the H atom on H-terminated Si(100)-3 × 1 surface moves to the radical chain under the influence of transition state by *ab initio* MD and periodic surface models. The calculated results agree well with experimental observations, and provide a H-abstractions procedure on H-terminated Si(100)-3 × 1 surface.

2. Computational details

Ab initio MD simulations were performed using the program CASTEP [37] on cells with periodic boundary conditions. This code employs DFT using a plane-wave basis set with Vanderbilt ultrasoft pseudo potentials to approximate the interactions between core and valence electrons. The exchange-correlation energy was calculated using the Perdew–Burke–Ernzerhof (PBE) modification to the generalised gradient approximation. Our plane-wave basis set had a cutoff of 280 eV. We carried out constant volume – constant temperature (NVT) runs, with the temperature controlled using a Nośe–Hoover thermostat [38,39]. In [40], both spin-unpolarised and spin-polarised calculations are performed to get the energy and structure about the reaction of C_2H_2–a H-terminated Si(111) surface. They found that both calculations can give the very similar conclusion for most of the pathway, and there are nonnegligible differences in the activation barriers. Thus, in our calculation, the more realistic spin-polarised calculations are selected.

In this paper, the cell size chosen contains a slab of four silicon layer and one ethylene molecule, and the size parameters are set to 7.68 × 11.52 Å *xy*-plane. Molecules are absorbed on the upper surface of the slab, where a monolayer of H atoms is also present to saturate part of the Si dangling bonds. And on the slab's bottom surface, all Si dangling bonds are also saturated by H atoms. In calculations, the two lowest Si layers of the slab and the saturating H atoms are fixed at the ideal positions to simulate a bulklike environment (and the Si—H distance was previously optimised). In the geometry optimisations, the residual forces acting on all mobile atoms are always smaller than 10^{-4} atomic units. In the simulation, charge neutrality is achieved through the use of a uniform neutralising background. A time step of 0.5 fs was required for the calculations. The cubic cell dimensions were fixed at the values for ambient conditions in all calculations. And the equilibrated structure was generated by performing 50 ps classical MD calculations using COMPASS force field [41,42] at the beginning of *ab* MD.

To determine the reaction pathways and activation energies, we have applied the LST method [36] in the context of CASTEP. This method is a common approach of interpolating geometrically between a reactant and a product to generate a reaction pathway. It can be used, in conjunction with single point energy calculations (using DFT), to perform transition state searches. Strictly speaking, the transition states from LST method are not also natural ones. Like the String method [43], the LST method yields a structure which is close to the true transition state [44]. In order to show the reaction pathway, we still call the structure at saddle point in the energy profile as transition state in the following. With the LST method, one seeks to determine the minimum energy pathway in a reaction where both the initial (reactant) and final (product) states are known. An idealised set of structures connecting reactants and products is obtained by linearly interpolating the distances between pairs of atoms in the reactant and product according to:

$$r^{i}_{ab}(f) = (1 - f)r^{\mathrm{R}}_{ab} + f r^{\mathrm{P}}_{ab} \qquad (1)$$

where r^{R}_{ab} and r^{P}_{ab} are the inter-nuclear distances between the pair of atoms *a* and *b* in the reactant (R) and the product (P), respectively; and *f* is an interpolation parameter which varies between 0 and 1. Halgren and Lipscomb [36] define the LST path by finding the molecular geometry with inter-nuclear distances as close as possible to the idealised values.

This is obtained by minimising the function S:

$$S(f) = \frac{1}{2}\sum_{a\neq b}\frac{\left[r_{ab} - r^{i}_{ab}(f)\right]^{2}}{\left[r^{i}_{ab}(f)\right]^{4}} + 10^{-6}\sum_{a}\left[x_{a} - x^{i}_{a}(f)\right]^{2}, \qquad (2)$$

where x^i_a is the interpolated Cartesian position of an atom and x_a is the actual coordinate. A local maximum on the reaction path is a saddle point and thus corresponds to a transition state of the reaction. The function S is necessarily always greater than or equal to zero and the reactant and product geometries therefore minimise S when f is 0 and 1, respectively. The LST pathway is generated by computing the geometries for several values of f. The number of values used is determined by the *number of frames* specified, and in our calculation 10 frames are selected. In order to use the method in periodic system, a modified functional form for S is used, in which a cutoff radius is introduced. The cutoff radius causes the contribution to S to reduce gradually to zero.

3. Results and discussion

3.1 Reaction pathways of ethylene molecule on H-terminated Si(100)-3 × 1 surface

Using LST method, one potential energy profile and selected configuration along the minimum energy pathways for the addition of ethylene molecule to a H-terminated Si(100)-3 × 1 surface in 7.68 × 11.52 Å^2 *xy*-plane are shown in Figure 1(a). This pathway consists of two parts separated by an intermediate metastable state (a local minimum in the system's potential energy surface). One is from the initial reactant to the intermediate state, and the other is from the intermediate state to the final product. Both are determined by performing two separate LST calculations, each involving 10 frames. For the first part, the initial state is a configuration in which the ethylene molecule are located at a distance of 15 Å above the H-terminated Si(111) surface. And in the initial state, the ethylene molecule has the tilt angle 35° with the *xy*-plane of Si(111) surface. When the distance between the molecule and the surface is about 15 Å, we think that they are completely decoupled, for example the C—C and C—H distances in the molecule are the same as the isolated molecule, and thus the initial relative orientation of the molecule is not important [42]. According to our previous simulation about the alkyl chain on Si(111) surface, the tilt angle of octane chain with the surface is about 35° [34]. In Figure 1, the intermediate state (the inset c) corresponds to a Si—CH$_2$—CH$_2^{\cdot}$ radical and no Si dangling bond's present on the surface. This state has 0.45 eV more stable than the initial one, while the final state (the inset e) is about 1.47 eV more stable than the initial one. In the final state, the original Si db site is replaced by the Si—CH$_2$—CH$_3$, and a new Si dangling bond is formed at a nearest neighbour surface site.

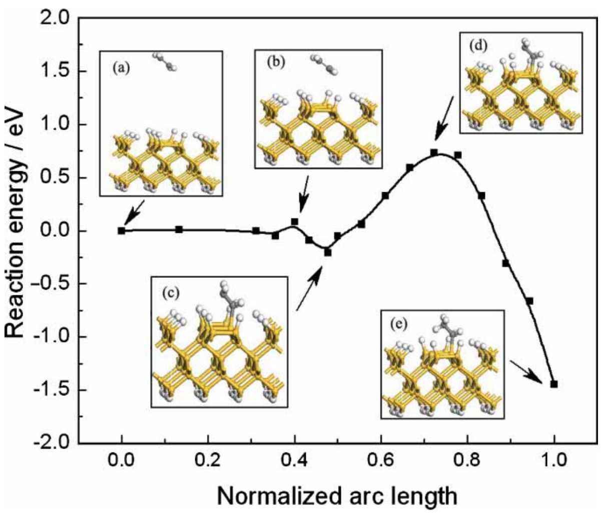

Figure 1. Potential energy profile along the minimum energy pathways for the reaction of ethylene with the H-terminated Si(100)-3 × 1 surface. The zero of energy corresponds to the noninteracting surface + molecule system. Silicon atoms are yellow, carbons are grey and hydrogens are white.

In Figure 1, we note that the ethylene molecule has to overcome a small energy barrier (0.1 eV) to attach to the surface and reach the intermediate metastable state. This energy is related to the breaking of C═C bonding in the ethylene molecule and the structure change of carbon atom from sp^2 to sp^3 in hybridisation. Due to the very low barrier, it is very easy to get the intermediate metastable state from the initial state. From the intermediate state (the inset c) to the final state, the reaction involves the hydrogen abstraction, so a high activation barrier is 0.71 eV (the inset d, transition state). Since the second barrier is higher the first barrier, this process represents the reaction rate of ethylene with the Si surface [40].

In order to observe the formation and breaking of bonds during the reaction of the molecule with the Si(100)-3 × 1 surface, the electronic charge densities in the reaction pathway were shown in Figure 2. In Figure 2, we only consider the active Si atom and another additional neighbour Si atom near the second transition state. The total electronic charge density in the initial state, shown in Figure 2(a), clearly shows the strong C═C bonding interaction. When the molecule locates above the surface, the charge density of the intermediate metastable and the transition state has been changed drastically (Figure 2(c),(d)). The reduction of C—C bonding electron density is observed, and the clear C—Si bonding election density is shown in Figure 2(c),(d). Especially in the transition state (Figure 2(d)), the H atom is located at the position among the C atom and the nearest neighbour Si

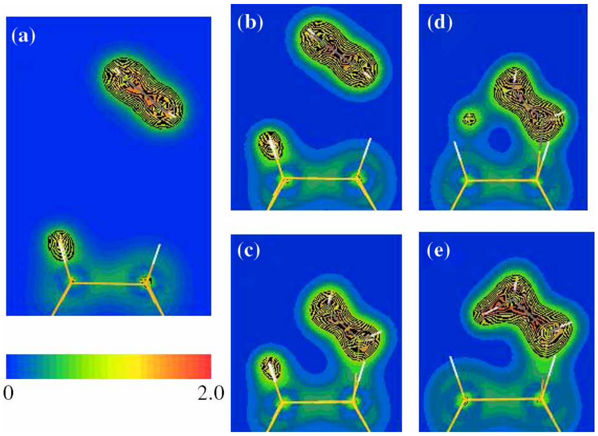

Figure 2. The charge densities in a plane perpendicular to the surface and passing through the C—C molecular bond. The inset symbols marked as (a)–(e) refer to the states in the inset of Figure 1.

atom. It represents the breaking of Si—H bond and the form of C—H bond. These charge densities show the abstraction of the hydrogen atom from the nearest neighbour Si atom at the surface.

The closely packed structure of alkyl chain on Si(100)-3 × 1 surface is a quadrangular lattice (Figure 3(a)). When ethylene molecules are chemisorbed on Si(100)-3 × 1 surface, possible H-abstraction orientation for the Si atoms is from the nearest neighbours (NN, or the first neighbours) or the next-nearest neighbours (NNN, or the second neighbours). To search for the idea reaction pathway, we get the potential energy profile along the minimum energy pathways from the NN or NNN Si atom using the LST method. For the $Si{-}CH_2{-}CH_2^{\cdot}$ radical in the central Si atom, since there are different H atoms on the nearest or next-nearest neighbour Si atoms which can be abstracted, we defined NN1, NN2, NN3 nearest neighbours and NNN1, NNN2 next-nearest neighbours, respectively, as showed in Figure 3(a). These different potential energies along the minimum energy pathways are shown in Figure 3(b). We note that the energy barrier along NN1 reaction pathway is 1.23 eV lower than those along other reaction pathways, such as NN2 (1.94 eV), NN3 (2.93 eV), NNN1 (1.52 eV) and NNN2 (2.79 eV). It means that the H-abstraction from nearest-neighbour Si atom (NN1) is easy in the reaction. It is our reason that the reaction pathway along NN1 was selected to show the charge densities in Figure 2. We note that the distance of two-neighbour Si atoms along NN1 pathway (2.36 Å) is shorter than that along NN2 (3.84 Å) or NN3 (5.32 Å). It is easy to understand, this is the effect of the larger distance between the H adatom and the unpaired electron of the radical for the different reaction pathways.

We also note that the distance of NNN1 (4.51 Å) is longer than that of NN2 (3.84 Å), however, the energy barrier along NNN1 reaction pathway (1.52 eV) has the second reaction pathway. We deduce that the alkyl chain ($-CH_2-CH_3$) should be along the direction between the NN1 and NNN1. On the other word, the final conformation of alkyl chain will locate the position between NN1 and NNN1 Si atoms, although the initial H-abstraction may be happened along the direction of NN1. The next *ab initio* MD trajectory will confirm the deduction. The energy barriers along NN3 and NNN2 reaction pathways are more than 2.7 eV. It means that the H-abstraction form the next-nearest neighbour Si atoms are difficult in the reaction, and we deduce another H-atom on these Si atoms can affect the H-abstraction.

3.2 *Reaction dynamics of alkene molecules on Si(100)-3 × 1 surface*

To address the dynamics of H-abstraction on Si(100)-3 × 1 surface, another *ab initio* MD was carried out for the transition state (the "d" structure in Figure 1). Analysis

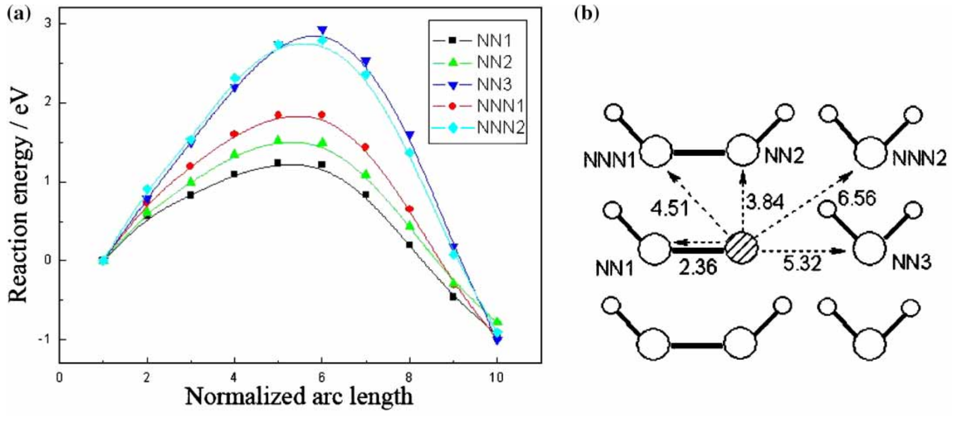

Figure 3. Potential energy profile along the minimum energy pathways for H-abstraction from nearest neighbour Si atoms and next-nearest neighbour Si atoms in 7.68 × 11.52 Å *xy*-plane, starting from geometry intermediate metastable state to the final state. The zero of energy corresponds to intermediate metastable state.

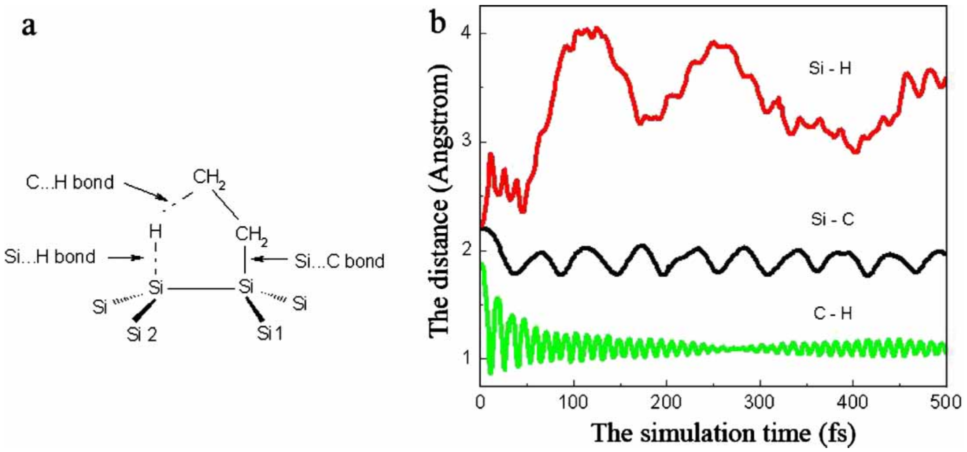

Figure 4. Time evolution of selected C···H, Si···H, and Si···C interatomic distances for transition state of Si(100) surface bond organic group with a carbon-centered radical.

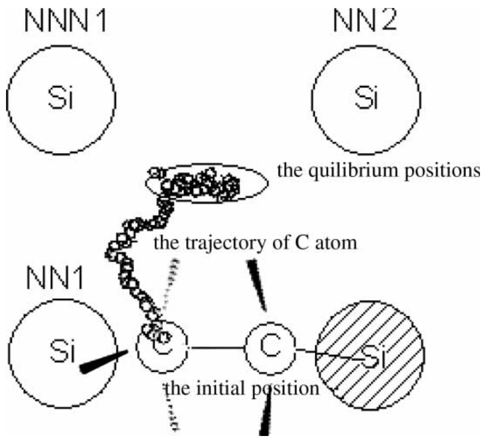

Figure 5. The trajectory of alkyl chain with time evolution.

of the MD simulation showed that the C···H bond is being formed and the Si···H bond is being broken. Figure 4 presents the dynamics of selected intermolecular C···H distance, Si···H distance and the changes of Si···H distance with time evolution. The particular example of intermolecules has been chosen to demonstrate different situations on the dynamics of the system. One can see the formation of C···H bond and the break of Si···H bond due to translational and large-amplitude rotational motions. In *ab initio* MD, the C···H bond is formed in a very short time from the transitional state. The Si···H distance is bigger than the chemical bond length of Si···H, and increases with time evolution. The Si···C bond between the Si surface and the alkyl chain oscillates.

Table 1. Comparison of optimised structural parameter (bond lengths (Å) and angles (deg)) values for ethylene adsorbed on Si(100) surface.

Parameter	Our work	Ref. [45]†	Ref. [46]‡
Bond C—C	1.54	1.52	1.62 ± 0.08
Bond C—Si	1.89	1.93	1.90 ± 0.04
Bond Si—Si	2.36	2.33	2.36 ± 0.21
Angle C—C—Si	118.56	103	101 ± 3
Torsion C—C—Si—Si	72.64		–

† Calculated results from the reference [45]. ‡ Experimental results in parentheses [46].

Because the initial model conditions may have some influence on the results, particularly the location of the end of carbon atoms in the hydrogen chain. Additional studies are therefore necessary by varying the initial arrangements of the alkyl chain, to eliminate possible artifacts. In *ab initio* MD, we concentrate on the dynamic move of the alkyl chain form the initial structure with time evolution. In order to show the trajectory of the carbon atom on Si surface, the positions of carbon atom of head group are shown in Figure 5. We note that after 240 fs, the methyl group will be oscillated round the equilibrium position. It means that, although the initial condition may influence the final result, the statistically more accurate conclusions about the final structure can be obtained through *ab initio* MD with time evolution. In our calculation, the final optimised structure is that the torsion Si—Si—C—C is 72.64°. The Si—C bond is 1.89 Å, and the angle of C—C—Si is 118.56°, respectively. Table 1 lists the main structural parameters of the ethylene adsorbed on Si(100) surface. We note that our results are similar to the other works. It shows that LST and *ab initio* MD methods can give the reliable results for the ethylene molecules adsorbed on Si(100) surface.

4. Conclusions

The structure and short-time dynamics of H-abstraction and reaction pathway about an alkyl chain on Si(100)-3 × 1 surface were studied by means of LST and *ab initio* MD simulations. LST method shows that (1) the ethylene molecule has to overcome a small energy barrier to the intermediate metastable state. This energy barrier is related to the breaking of C═C bonding in the ethylene molecule and the structure change of carbon atom from sp^2 to sp^3 in hybridisation and (2) the nearest neighbour (NN, or the first neighbours) Si atom in the same dimer favors to possible H-abstraction orientations in contrast to the other NN or next-nearest neighbours (NNN, or the second neighbours) Si atoms on Si(100)-3×1 surface. Our results are in agreement with the available experimental observations and provide the information on the reaction pathways and barriers. It confirms that the reaction occurs via an intermediate state with lower potential energy than the noninteracting molecule + surface system, and the intermediate state is characterised by the presence of a carbon-based radical.

From the intermediate state, *ab initio* MD was used to investigate the H-abstraction on Si(100)-3×1 surface bound organic group with a carbon-centered radical, *ab initio* MD shows that the C···H bond is formed in a very short time from the transitional state. At the same time, the Si···C bond between the Si surface and the alkyl chain oscillates with time evolution.

Acknowledgements

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